Mineral weathering rates coupled to bedrock fracturing and saprolite formation

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Spheroidal weathering is a common mechanism by which bedrock corestones disaggregate to form saprolite. In the Rio Icacos watershed in the Puerto Rican rainforest, quartz diorite bedrock weathers spheroidally, producing a 0.2-2 m thick zone of concentric, partially weathered rock layers (~2.5 cm each) called rindlets. Sperhoidal fracturing has been modeled to occur when a weathering reaction with a positive ΔV of reaction builds up elastic strain energy (Fletcher *et al*., 2006). The rates of spheroidal fracturing and saprolite formation are therefore controlled by the rate of the weathering reaction.

Based on petrographic evidence and thermodynamic calculations, we have identified biotite oxidation as the most likely fracture-inducing reaction. Oxidation of Fe(II) within the biotite lattice occurs with a concomitant loss of interlayer K^+ to maintain charge balance. Adsorption of water to the interlayer could produce a positive ΔV of reaction sufficient to initiate fracturing if it occurs before other weathering reactions increase porosity enough to relieve the stress generated. Thus, detection of incipient weathering reactions is crucial for identifying the rate-controlling reaction.

Evidence for progressive biotite oxidation across the rindlet zone was inferred from the decreasing K content of the biotites and by decreasing Fe(II) content in bulk samples of the rindlets. Using a 1-D linear model (White, 2002) of the gradient in Fe(II), we calculated a biotite oxidation reaction rate of 7.2×10^{-14} mol $m^{-2}s^{-1}$. Evidence for incipient biotite oxidation was documented within the bedrock corestone by hard X-ray microprobe mapping and XANES, both performed at Beamline 2-3 at the Stanford Synchrotron Radiation Laboratory. Maps of Fe(II) and Fe(III) at 2 µm resolution revealed oxidized zones within individual biotite crystals. This ability to map oxidation states within individual crystals holds promise for identifying incipient weathering reactions within "pristine" bedrock, which in turn will allow quantification of rate limiting reactions in coupled processes such as spheroidal weathering.

References

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Paradox of the plankton: Why is Proterozoic export production dominated by cyanobacteria?

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Eukaryotic organisms are well documented in the fossil record from at least the Mesoproterozoic, but the distribution of 2-methylhopanoid biomarker molecules suggests that cyanobacteria continued to dominate marine productivity until the Phanerozoic (Summons, R. E., *et al*. 1999. *Nature* **400**:554–557). Although poorly resolved, the switchover to modern-style, eukaryote dominated export production can be broadly linked to the early Cambrian (Tommotian) "explosion" of animals, trace fossils and small ornamented acritarchs, the latter reasonably interpreted as the cysts of eukaryotic phytoplankton. The coincidence of these various signatures points to a fundamemetal shift in marine ecology.

The subdued expression of pre-Cambrian algae has been attributed to nitrogen limitation associated with a sulphidic deep ocean, but this is not supported by recent experimental results (Zerkle *et al*. 2006. *Geobiology* **4**:285–297). Nor can the switch be simply attributed to appearance of eumetazoans, which precede the Cambrian explosion by some hundred million years and appear to have been exclusively benthic. The first real opportunity for eukaryotic phytoplankton came as metazoans moved into the water column to graze directly on primary productivity. In the absence of predation, unicellular phytoplankton are expected to evolve to minute size, without morphological elaboration, playing strongly to the strengths of cyanobacteria. The key to eukaryotic success, however, lies in their capacity for morphological differentiation, in this case the diverse ornamentation of early Cambrian acritarchs serving to frustrate grazing mesozooplankton. By selectively removing the long-standing cyanobacterial incumbents – and providing the trophic link between unicelluar phytoplankton and macrometazoans – mesozooplankton can be held responsible for uniquely eukaryotic expression of the Phanerozoic biosphere.